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Magnetic measurement and crystal-field analysis of the optical and magnetic data of $Tm_2(SO_4)_3.8H_2O$ crystal

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Abstract The measurements of the mean magnetic susceptibility and crystalline anisotropy of $Tm_2(SO_4)_3.8H_2O$ have been carried out in the temperature range 80-300 K. The results of magnetic measurements are explained using a crystal field of C_{1h} symmetry which is the major symmetry confirmed by optical absorption, Zeeman spectroscopy and para electric resonance experiment. All the results show nearly accidentally degenerate Stark components in the ground state and the presence of the nearly degenerate pair of Stark component within 0.57 ± 0.1 cm^{-1} in the ground manifold. A set of crystal field parameters are evaluated using a rigorous approach and making consistent interpretation of both the magnetic and optical data.

Keywords Crystal-field parameters, magnetic and optical data, $Tm_2(SO_4)_3.8H_2O$ crystal

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1. Introduction

We present both theoretical and experimental investigations of the magnetic susceptibility and its variation with temperature of thulium sulphate octahydrate crystal. Specifically, we have measured the mean magnetic susceptibility together with the principal magnetic susceptibilities (crystalline) and hence, the anisotropies over the temperature range 80-300 K. So far, no crystal field analysis of this crystal has been performed. However, from a study of the optical absorption spectra of single crystal of $Tm_2(SO_4)_3.8H_2O$, Karlow and Gruber [1] have suggested a low symmetry C_{1h} of the crystal field. Using this symmetry, we intend to analyse the magnetic data that we have obtained. It is important to note that this spectroscopic work indicates a nearly accidental degeneracy in the ground state of tripositive thulium in the octahydrated sulphate salt which has been supported by Zeeman spectroscopy and paraelectric resonance experiments. The degenerate ground level consists of two nearly degenerate ground singlets within 0.57 ± 0.1 cm^{-1}.

Our purpose is to investigate whether it is possible to find a single set of parameters remaining within the same theoretical framework for both magnetic and optical data mentioned above. The specific properties we would try to correlate are the Sark splitting of excited levels, the accidentally degenerate ground level, the observed spectroscopic splitting factor and the magnetic anisotropies over the entire temperature range. The theoretical model that we use, implies the most rigorous approach of direct diagonalisation of the Hamiltonian in a complete basis of states belonging to all the terms of the Tm^{3+}-ion. This method has the advantage that it automatically includes intermediate coupling and different J-mixing under the crystal field. Finally, it may be mentioned that the present theory with a set of fifteen parameters, provides a fair overall description of the magnetic and the optical data.

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2. Experimental methods

Powdered sample of Tm-sulphate octahydrate was dissolved in ice cold water. Crystals are formed by very slow evaporation of the solution in a dry atmosphere. For facilitating crystalization few drops of concentrated H_2SO_4 acid are also added to the solution. Crystals are needle shaped about $(5 \times 1 \times 1)$ mm in size and colourless. For susceptibility measurement, the crystals are finely ground.

The crystals are monoclinic with space group C_{2h}^6, dimensions [2] of the unit cell are $a = 18.12$ Å, $b = 6.67$ Å, $c = 13.43$ Å and the monoclinic angle $\beta = 101°57'$. The symmetry

(diad) axis is along b. One of the three principal crystalline susceptibilities χ_1, χ_2, χ_3 lies along the symmetry axis and it is denoted by χ_3, χ_1 and χ_2 lie in the ac plane, χ_1 being taken to be greater than χ_2 by convention. For uniaxial symmetry of the ion, the principal ionic susceptibilities are denoted by $K_\parallel$ and $K_\perp$ which lie parallel and perpendicular to the symmetry axis z respectively *i.e.* $K_\parallel = K_z$, $K_\perp = K_x = K_y$.

Bleaney *et al* [3] gives the correlation between ionic and crystalline magnetic anisotropies in a monoclinic crystal with uniaxial symmetry. There are two sets of equations [3, 4] depending upon whether $K_\parallel$ is greater or less than $K_\perp$. For thulium sulphate octahydrate crystals experimental results indicate that $K_\parallel > K_\perp$ at all temperatures. Noting that there are two rare earth ions per formula unit, the relevant relations for thulium sulphate octahydrate are given as follows :

$$K_\parallel - K_\perp = (\chi_1 - \chi_2) - \tfrac{1}{2}(\chi_1 - \chi_3), \tag{1a}$$

$$\cos 2\phi = (\chi_1 - \chi_3)/[2(\chi_1 - \chi_2) - (\chi_1 - \chi_3)]. \tag{1b}$$

Eq. (1b) is used to test whether $K_\parallel > K_\perp$ using experimental principal crystalline susceptibility values. Further, the general relation between the crystalline and mean ionic susceptibilities is

$$\bar{K} = (K_\parallel + 2K_\perp)/3 = \bar{\chi}/2. \tag{2}$$

The macroscopic habit of the crystal is such that no crystallographic planes or axes other than the symmetry axis b could be identified. Hence magnetic measurements were done by adopting the method as detailed in our previous communication [5]. The temperature was kept steady within ± 0.1K. The estimated accuracy of the susceptibility measurement is ~ 5%.

3. Theoretical calculation

The effective Hamiltonian for the crystal field energy level calculation of Tm^{3+} ion in the absence of external field is taken to be consisting of electrostatic energy H_r'' corresponding to inter electronic repulsion energy, the spin orbit interaction energy H_{so} and the crystal field energy H_{cf} only. Thus,

$$H_{eff} = H_r'' + H_{so} + H_{cf}. \tag{3}$$

Taking the point group symmetry of the Tm^{3+} ion to be C_{1h}, the crystal field Hamiltonian is written in terms of tensor operators C_q^k as defined by Judd [6] and Wybourne [7] as

$$H_{cf} = \sum_{\substack{j \\ k=2,4,6 \\ 0<q\le k}} \left\{ B_{k0}\left(C_0^k\right)_j + B_{kq}\left[\left(C_q^k\right)_j + \left(C_{-q}^k\right)_j\right] + iB_{k-q}\left[\left(C_q^k\right)_j - \left(C_{-q}^k\right)_j\right]\right\}. \tag{4}$$

where the sum over j includes all the $4f$ electrons. Terms involving both odd q and even k are not allowed for C_{1h} point group symmetry [6,7] and there exist fifteen crystal field parameters. The matrix of the total Hamiltonian is constructed taking all the states arising out of all the atomic terms [7] of f^{12} ion as the basis states in the $|S\,L\,J\,J_z\rangle$ scheme. The energy matrix of Tm^{3+} ion comes out to be of the order of 91 × 91. The matrix is then diagonalized with the help of a computer (vax 3400). The fifteen crystal field parameters B_{kq}'s are adjusted to fit the observed crystal field splittings and magnetic data with the calculated ones. The diagonalization yields thirteen Stark levels for the ground term. The next higher multiplet is of the order of 5350 cm^{-1} above the ground multiplet. The significant contribution to the magnetic susceptibility comes from the lowest group of thirteen levels resulting from the diagonalization procedure. Zeeman perturbation is now applied on these states and the paramagnetic susceptibility upto second order along and perpendicular to the symmetry axis of the ion at different temperatures is calculated using Van Vleck's formula [8].

4. Results and discussion

Only eight [SL]-J levels are identified including $^3P_{2,1,0}$, $^1D_2$, $^1I_6$, $^3F_{3,2,1}$ in the optical absorption experiment, the level $^1S_0$ is too high in energy to be observed, the spectra of $^3H_4$ and $^3H_5$ levels are obscured by the absorption due to the water molecules in the octahydrate complex, the Stark levels of the ground $^3H_6$ manifold were deduced from the temperature dependent spectra. Consequently, no crystal field analysis of the Stark splittings was performed. However, in our calculation we have considered all the levels arising out of all the atomic terms of f^{12} ion. We have evaluated the crystal field parameters from our magnetic susceptibility data consistent with available spectral data and maintaining fair agreement between theoretical and observed values of separation between the nearly degenerate ground singlets in the ground manifold and the observed spectroscopic splitting factor. After an extensive trial, we arrived at the following set of parameters which gives the best possible fit to magnetic data, available Stark splittings and also explains the spectroscopic splitting factor and the separation between the nearly degenerate ground singlets.

E^1 = 6606.9885 cm^{-1}	E^2 = 34.581 cm^{-1}
E^3 = 667 9935 cm^{-1}	ξ = - 2700 cm^{-1}
B_{20} = 661.52 ± 22 cm^{-1}	B_{22} = 359.78 ± 21 cm^{-1}
B_{2-2} = 34.82 ± 12 cm^{-1}	B_{40} = 440 00 ± 31 cm
B_{42} = 314 28 ± 4 cm^{-1}	
B_{4-2} = - 1100 00 ± 6 cm^{-1}	B_{44} = - 383.43 ± 5 cm^{-1}
B_{4-4} = 209.52 ± 8 cm^{-1}	B_{60} = 712.10 ± 10 cm^{-1}
B_{62} = 51.58 ± 15 cm^{-1}	B_{6-2} = 500.39 ± 12 cm^{-1}
B_{64} = 307.93 ± 5 cm^{-1}	B_{6-4} = 115.47 ± 2 cm^{-1}
B_{66} = 230.18 ± 12 cm^{-1}	B_{6-6} = -159.36 ± 14 cm^{-1}

The observed mean susceptibility values of the powdered sample together with the experimentally observed χ_1 and χ_3 values of Tm – sulphate octahydrate crystals at different temperatures are shown in Figure 1. The agreement between the observed and theoretically computed thermal variation of the mean ionic susceptibility $\bar{K}$ and principal ionic susceptibilities $K_\parallel$ and $K_\perp$ are shown in Figure 2. The figure shows that the agreement is fairly good for all three quantities. The deviation of the calculated values from the observed ones are (0.6% – 7.5%), (2.2%–9.1%) and (2.1% – 10.0%) for $\bar{K}$, $K_\perp$ and $K_\parallel$ respectively, within the temperature range of 300 to 80K.

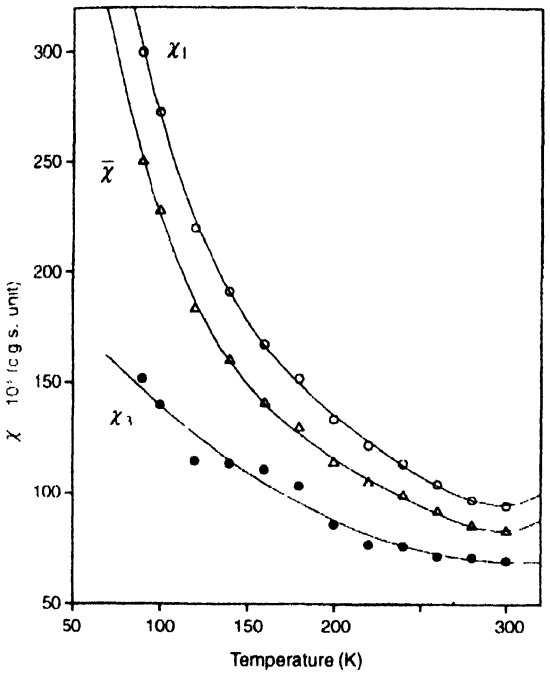

Figure 1. Thermal variation of $\bar{\chi}$, χ_1 and χ_3 for thulium sulphate octahydrate Δ experimental points of χ , O– experimental points of χ_1, • experimental points of χ_3 (Solid lines are fit to aid the eye)

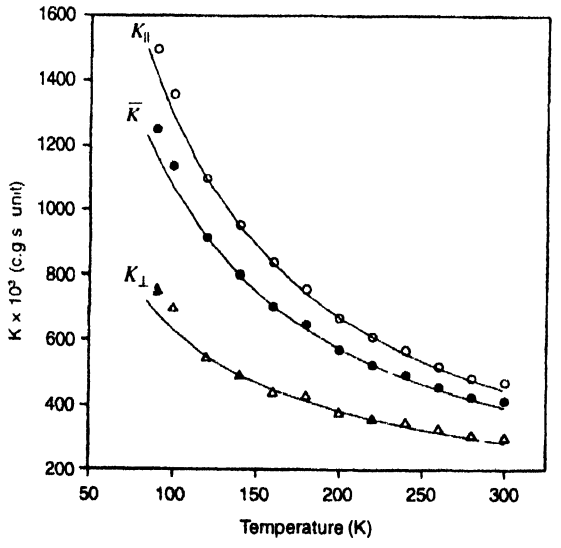

Figure 2. Thermal variation of mean ionic susceptibility $\bar{K}$ and principal ionic susceptibilities $K_\parallel$ and $K_\perp$ for thulium sulphate octahydrate. — theoretical curve. Δ– experimental points of $K_\perp$, O– experimental points of $K_\parallel$. •– experimental points of $\bar{K}$.

The calculated first order crystal field splittings together with available observed splittings for the J manifolds are given in Table 1. The values of the calculated and observed seperation Δw (say) between the ground singlets are quoted below for comparison

$$\Delta w \text{ (observed)} = 0.57 \pm 0.01 \text{ cm}^{-1},$$

$$\Delta w \text{ (calculated)} = 0.5756 \text{ cm}^{-1}.$$

Table 1. Crystal field splitting of $Tm_2(SO_4)_3 \cdot 8H_2O$

^{2S+1}LJ level	Empirical label	Experimental energy levels (cm^{-1})	Center of gravity (cm^{-1})	Relative observed splittings (cm^{-1})	Relative calculated splittings (cm^{-1})
$^3H_6$	Z_1			0	0
	Z_2			0 57	0 549
	Z_3			102	101 3
	Z_4			243	103 6
	Z_5			255	277 8
	Z_6			309	310 6
	Z_7			363	361 9
	Z_8			437	389 3
	Z_9			461	404 5
	A_1	12623	12778 5	-155 5	-183 8
	A_2	12648		-130 5	-167
	A_3	12742		36 5	-121 8
	A_4	12755		-23 5	-53 9
	A_5	12767		-11 5	18 7
	A_6	12803		24.5	-1 2
	A_7	12835		56 5	129 4
	A_8	12899		120 5	151 3
	A_9	12935		156 5	265 8
	B_1	14512	14580	-68 3	-110 2
	B_2	14573		-7 3	0 3
	B_3	14576		-4.3	3 0
	B_4	14579		1 3	18 2
	B_5	14583		2.7	18 3
	B_6	14601		20 7	31 3
	B_7	14638		57.7	39 0
$^3F_2$	C_1	15134	15213	-79.6	-55 9
	C_2	15161		-52.6	-44 0
	C_3	15207		-6 6	-27.1
	C_4	15268		54 4	58 4
	C_5	15298		84 4	68 4

Table 1. *Cont'd*

^{2S+1}LJ level	Empirical label	Experimental energy levels (cm^{-1})	Center of gravity (cm^{-1})	Relative observed splittings (cm^{-1})	Relative calculated splittings (cm^{-1})
$^1D_2$	E_1	27934	28013.4	-79 4	-55 9
	E_2	27971		-42 4	-44 0
	E_3	28007		-6 4	-27 1
	E_4	28075		61.6	58.4
	E_5	28080		66.6	68.4
$^1P_1$	H_1	36420	36495 7	-75 7	-90.7
	H_2	36464		-31.7	6.2
	H_3	36603		107 3	83.8
$^1P_2$	I_1	38092	38234	-142	164 2
	I_2	38146		-88	128 9
	I_3	38230		-4	-24 2
	I_4	38326		92	-122 1
	I_5	38376		142	-146 6

Next, we proceed to calculate the spectroscopic splitting factor. Karlow and Gruber [1] has confined the nearly degenerate ground singlets in the ground manifold of Tm sulphate octahydrate by Zeeman spectroscopy [1] and PER experiments [1]. From Zeeman measurements, they inferred that the Zeeman splittings in $Tm_2(SO_4)_3.8H_2O$ is due entirely to the magnetic interaction between the nearly degenerate ground Stark levels. The spectroscopic splitting factor calculated from their experiment yields the value 13.4 L.U for the splitting factor. We have calculated theoretically the first and second order Zeeman energies of the two nearly degenerate ground Stark levels. After introducing the magnetic interaction the energy values W_1, W_2 of the two levels upto second order in energy are given by

$$W_1 = W_1^{(0)} + 6.124810\beta H - 1.957505(\beta H)^2,$$

$$W_2 = W_1^{/(0)} - 6.120041\beta H - 1.954813(\beta H)^2,$$

where $W_1^{(0)}$ and $W_1^{/(0)}$ are the Stark energies of the two components in the absence of magnetic field H. Remembering that these two nearly degenerate levels were initially separated by a small amount (~ 0.5756 cm^{-1}) in zero magnetic field, the additional splitting between these two levels due to Zeeman interaction only comes out to be 12.24215 L.U.

However, we may conclude that though the assumption of C_{1h} symmetry for Tm- sulphate octahydrate is very approximate one, the crystal field parameters evaluated on the basis of this symmetry, can more or less explain the magnetic data, available optical data and Zeeman splitting.

Acknowledgment

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